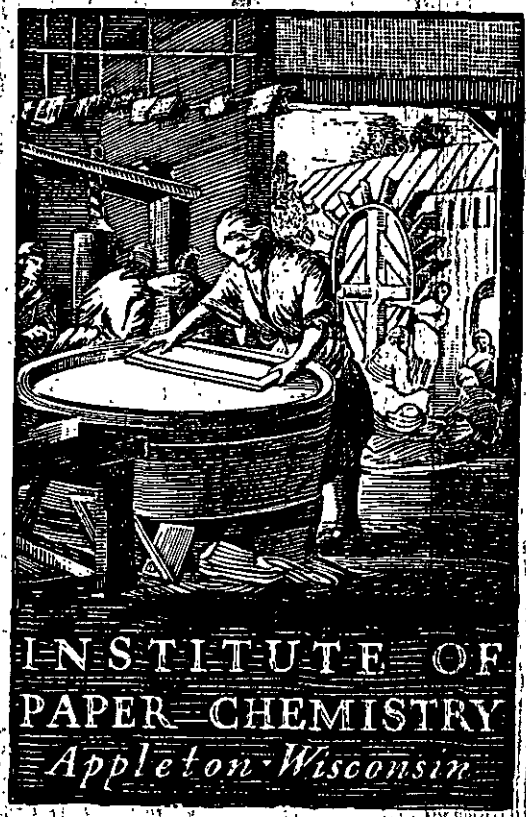

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

CHLORINE DIOXIDE, ITS GENERATION AND COST

Research Grant

Project 2500

Report Seven

A Progress Report

to

THE GRANTORS

January 20, 1969

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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SUMMARY

The use of chlorine dioxide for the purpose of selective delignification appears to be more promising than other known oxidants in the present development of holopulping. Incorporating caustic treatments, the process is capable of producing a versatile pulp at high yields with relatively low consumption of the oxidant. If holopulping is to be realized in commercial practice, the cost of chlorine dioxide will be a controlling factor in the economics of the process. Recognizing this important point, we have followed closely the trends of chlorine dioxide generation both in practice and in research. This report presents the results of our survey from literature review as well as by private communications.

Thermal synthesis of chlorine dioxide from its elements is thermodynamically unfavorable. However, a photosensitized method of producing atomic chlorine and its reaction with ozone leading to the formation of chlorine dioxide is theoretically possible. Such a possibility is being investigated in our academic research.

The practical method of generating chlorine dioxide by reduction of electrolytically produced sodium chlorate has been considerably improved in the last few years, accompanied by significant lowering of cost. Among the commercial methods, the Day-Kesting process, using hydrochloric acid as the reducing agent, is most suitable for holopulping because its by-products, chlorine and hydrogen, can be fully utilized, directly or indirectly, in the pulping process. A recent version of this process patented by CHEMECH Engineering Ltd. appears to be

especially practicable for large-scale integrated sodium chlorate-chlorine dioxide production by virtue of improved efficiency and control. The complete process is described in some detail. Looking ahead, the possibility of electrolytic production of chlorine dioxide without the use of chlorate is also discussed.

By the CHEMECH process the total cost of chlorine dioxide for a plant of 50 tons per day is estimated at about 9 cents per pound based on electric cost of 6 mils per kw.-hr. With larger size and less expensive electricity, chlorine dioxide may be produced at as low as 6-7 cents per pound. At these costs of chlorine dioxide the cost of holopulp could become comparable to or even lower than that of kraft. A discussion of a complete holopulping process including chemical generation and recovery will be presented in a later report.

PREPARATION OF CHLORINE DIOXIDE

SYNTHESIS FROM GASEOUS ELEMENTS

Since chlorine and oxygen are relatively inexpensive chemicals, the feasibility of forming chlorine dioxide from its components should be examined in some detail. The overall reaction is

$$\frac{1}{2}\,Cl_2(g) + O_2(g) = ClO_2(g) \qquad (1)\ .$$

The thermodynamic functions for chlorine dioxide at the standard pressure of one atmosphere (ideal gas) and in the temperature range from absolute zero to 6000°K. have recently been compiled in JANAF Thermochemical Tables (1), from which the particular page for ClO_2 is reproduced as Table I. The reaction is endothermic, as indicated by the positive values of the standard heat of formation, and its equilibrium is, therefore, favored by increasing temperature. However, the equilibrium constant at 5700°K, is only about 10^{-4} atm.$^{-1/2}$, and its value is down to 10^{-6} at 1900°K.

That the formation of chlorine dioxide from the elementary gases is thermodynamically unfavorable may be further illustrated by equilibrium calculations. Since a high pressure promotes the yield of chlorine dioxide and a large excess of oxygen increases the conversion of chlorine, let the reaction conditions be 1900°K., 100 atm., and 100 moles of O_2 per mole of Cl_2 as the initial mixture. The yield of ClO_2 will be about 10^{-4} mole per mole of the initial Cl_2, or the conversion of Cl_2 about 0.005%! If air is used instead of pure oxygen, there will be at equilibrium more nitrogen oxides than chlorine dioxide.

ClO_2

CHLORINE DIOXIDE (ClO_2) (IDEAL GAS) MOL WT = 67.457

ΔH°_{f0} = 25 6 ± 1 5 kcal mole^{-1} $\Delta H^\circ_{f\ 298\ 15}$ = 25 ± 1 5 kcal mole^{-1}

Point Group C_{2v} $S^\circ_{298\ 15}$ = 61 453 cal deg^{-1} mole^{-1}

Vibrational Levels and Multiplicities

ω, cm^{-1}
945.3 (1)
447 4 (1)
1109 (1)

Electronic Level and Multiplicity

ϵ_i, cm^{-1}	g_i
0	2

No α_i available. σ= 2

Rotational constants: A_{000} = 1.6006 cm^{-1}, B_{000} = 0 53283 cm^{-1}, C_{000} = 0.27553 cm^{-1}

X_{11} = -4 4 cm^{-1} X_{33} =-2 0 cm^{-1} X_{23} =-13 cm^{-1}

X_{22} = 0 X_{12} =-3 0 cm^{-1} X_{31} =-14 4 cm^{-1}

g_{22} = 0

Heat of Formation

H Evans, T R Munson, and D D Wagman, J Research Natl Bur Standards 55 147 (1955), have evaluated the available data and chosen the above value

Heat Capacity and Entropy

J S Gordon, private communication, February, 1961, has calculated the thermodynamic functions from 298 15° to 6000°K by the method of R E Pennington and K A Kobe, J Chem Phys 22, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account Gordon's data are from J B Coon and E Ortiz, J Molec Spectros 1, 81 (1957) The functions below 298 15°K have been calculated for a rigidly rotating harmonic oscillator

T, °K.	C_p°, cal mole^{-1}deg^{-1}	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$, kcal mole^{-1}	ΔH°_f	ΔF°_f	Log K_p
0	000	.000	INFINITE	- 2.582	25.590	25.590	INFINITE
100	8.085	51.762	69.612	- 1.785	25.326	26 560	- 58.043
200	8.997	57.623	62.293	- .934	25.134	27.472	- 30.455
298	10.039	61.453	61.453	.000	25.000	29.232	- 21.427
300	10.057	61.515	61.453	.019	24.998	29.259	- 21.314
400	11.011	64.544	61.860	1.074	24.928	30.691	- 16.768
500	11.744	67.084	62.657	2.213	24.909	32.135	- 14.046
600	12.279	69.275	63.582	3.416	24.922	33.580	- 12.231
700	12.669	71.199	64.535	4.664	24.953	35.020	- 10.933
800	12.957	72.910	65.477	5.946	24.995	36 455	- 9.958
900	13.176	74.450	66.390	7.253	25.042	37.885	- 9.199
1000	13.346	75.847	67.267	8.580	25.095	39.310	- 8.591
1100	13.480	77.125	68.106	9.921	25.148	40.728	- 8.091
1200	13.590	78.303	68.907	11.275	25.204	42.142	- 7.675
1300	13.681	79.395	69.673	12.639	25.259	43.552	- 7.321
1400	13.758	80 411	70.404	14.011	25.314	44.956	- 7.018
1500	13.824	81.363	71.103	15.390	25.369	46.357	- 6.754
1600	13.882	82.257	71.772	16.775	25.423	47.755	- 6.523
1700	13.933	83.100	72.414	18.166	25.477	49.150	- 6.318
1800	13.979	83.898	73.030	19.562	25.527	50.540	- 6.136
1900	14.021	84.655	73.622	20.962	25 575	51.929	- 5.973
2000	14.059	85.375	74.192	22.366	25 621	53.313	- 5.826
2100	14.095	86.062	74 741	23.774	25.665	54.698	- 5.692
2200	14.128	86.718	75.271	25.185	25.705	56.079	- 5.571
2300	14.159	87.347	75.782	26.599	25.744	57.458	- 5.460
2400	14.189	87.950	76.277	28.017	25.779	58.838	- 5.358
2500	14.217	88 530	76.755	29.437	25 809	60.213	- 5.264
2600	14.244	89.088	77.219	30.860	25.838	61.589	- 5.177
2700	14.270	89.626	77.669	32.286	25.863	62.965	- 5.096
2800	14.295	90.146	78.105	33.714	25.885	64.338	- 5.022
2900	14.320	90.648	78.529	35 145	25.904	65.711	- 4.952
3000	14.344	91.134	78.941	36.578	25.919	67.084	- 4.887
3100	14.367	91.604	79 342	38.013	25.932	68.457	- 4.826
3200	14 389	92.061	79.732	39.451	25.942	69.828	- 4.769
3300	14.411	92.504	80.113	40.891	25.949	71.198	- 4.715
3400	14.433	92.934	80.483	42.333	25.953	72 569	- 4.664
3500	14.454	93.353	80.845	43.778	25.956	73.939	- 4.617
3600	14.475	93.761	81.198	45.224	25.955	75.311	- 4.572
3700	14.496	94.157	81 543	46.673	25.953	76.682	- 4.529
3800	14 517	94.544	81.880	48.123	25.948	78.055	- 4.489
3900	14.537	94.922	82 210	49.576	25.943	79.423	- 4.451
4000	14.557	95.290	82.532	51 031	25.934	80.794	- 4.414
4100	14.577	95.650	82.848	52.488	25.924	82.167	- 4.380
4200	14.600	96.001	83.157	53.946	25.913	83.539	- 4.347
4300	14.614	96.345	83.460	55.407	25.901	84.912	- 4.315
4400	14.636	96.681	83.756	56.870	25.887	86.283	- 4.285
4500	14.655	97.010	84.047	58.335	25.872	87.655	- 4.257
4600	14.674	97.333	84 332	59 801	25 856	89 032	- 4.230
4700	14.693	97.648	84.612	61.269	25.839	90.406	- 4.204
4800	14.712	97 958	84 887	62.740	25.822	91 779	- 4.179
4900	14.731	98.262	85.157	64.212	25.805	93.150	- 4.154
5000	14.750	98.559	85.422	65.686	25.786	94.525	- 4.131
5100	14.768	98.852	85.683	67.162	25.767	95.901	- 4.109
5200	14.787	99.139	85.939	68.639	25.748	97 274	- 4.088
5300	14.806	99.420	86.190	70.119	25.729	98.655	- 4.068
5400	14.824	99 697	86 438	71.601	25.710	100.025	- 4.048
5500	14.843	99.969	86.682	73.084	25.691	101.407	- 4.029
5600	14 861	100.237	86.921	74.569	25.671	102 780	- 4 011
5700	14.879	100.500	87.157	76.056	25.652	104.157	- 3.993
5800	14.898	100.759	87 389	77.545	25.633	105.539	- 3.977
5900	14.916	101.014	87 618	79 036	25.615	106 914	- 3.960
6000	14.934	101.265	87 844	80.528	25.597	108.293	- 3.944

March 31, 1961

Table I. Thermodynamic Functions of Chlorine Dioxide

In spite of the unfavorable thermal formation of chlorine dioxide, the possibility of a photosensitized reaction exists. According to Morris and Johnston (2), when a mixture of Cl_2 and O_2 is photosensitized, the chlorine molecule dissociates into atoms which react with molecular oxygen to form a short-lived free radical Cl-O-O (peroxide), as distinguished from O-Cl-O (dioxide). The free radical then reacts with atomic chlorine to form chlorine monoxide which tends to degenerate into molecular chlorine and oxygen.

In the study of photosensitized decomposition of ozone by chlorine, Norrish and Neville (3) suggested a series of reactions, to summarize briefly:

$$Cl_2 + h\nu = 2Cl \qquad (2),$$

$$Cl + O_3 + O_2 = ClO_3 + O_2 \qquad (3),$$

$$2ClO_3(g) = Cl_2O_6(\ell) \qquad (4),$$

$$Cl_2O_6(\ell) = 2ClO_2(g) + O_2(g) \qquad (5)$$

In Reaction (2), $h\nu$ represents the energy absorbed by a molecule, h being Planck's constant and ν the frequency of the incident light. The standard free energy change for Reaction (3) at 25°C. is -16,650 cal./mole. It is further known that ClO_3 may be condensed into a liquid of Cl_2O_6 (4), and the latter may be thermally decomposed into chlorine dioxide and oxygen (5) in the absence of ozone. The last two equilibria (4) and (5) are also favorable, as indicated by the standard free energy changes of -8,630 and -13,900 cal /mole, respectively The kinetics of these reactions are being studied in a thesis (6) at the Institute The rate-controlling step is probably Reaction (3), which involves three-body collisions for the formation of chlorine trioxide.

GENERATION FROM SODIUM CHLORATE

At present, the practical method of generating chlorine dioxide remains to be the reduction of sodium chlorate. Rapson (7) has suggested that the underlying reactions for all known processes are the same, namely,

$$HClO_3 + HCl = HClO_2 + HClO \quad (6),$$

$$HClO_3 + HClO_2 = 2ClO_2 + H_2O \quad (7),$$

$$HClO + HCl = Cl_2 + H_2O \quad (8).$$

The difference among the major processes is in the choice of reagents, as shown in Table II.

TABLE II

GENERATION OF ClO_2 FROM $NaClO_3$

Process	Acid (in excess)	Reducing Agent	By-products
Mathieson	H_2SO_4	SO_2	Na_2SO_4
Solvay	H_2SO_4	CH_3OH	Na_2SO_4
Hooker R-2	H_2SO_4	NaCl	Cl_2, Na_2SO_4
Day-Kesting	HCl	HCl	Cl_2, NaCl

For the holopulping purpose, both Na_2SO_4 and H_2SO_4 are undesirable components in the liquid effluent. By this criterion, only the use of hydrochloric acid will be considered. In this case, the effluent containing NaCl and the excess HCl may be reused in the electrolytic cells for producing $NaClO_3$. The chlorine generated with chlorine dioxide may be separated by their solubilities.

The reactions involved in the Day-Kesting process are represented by

$$NaClO_3 + 2HCl = ClO_2 + \frac{1}{2} Cl_2 + NaCl + H_2O \quad (9)$$

and

$$NaClO_3 + 6HCl = 3Cl_2 + NaCl + H_2O \quad (10) .$$

The undesirable reaction (10) may be kept at a minimum by a high concentration ratio of $NaClO_3$ to HCl. This is made practical by integrating ClO_2 generation with $NaClO_3$ production so that a partially reduced chlorate solution may be returned to the electrolytic cells for the reoxidation of sodium chloride.

The Day-Kesting process as once practiced at Brown Company, N.H., was rather inefficient and difficult to control. Its reduction efficiency seldom exceeded 70%, while the other processes attained efficiencies over 90%. A recent modification of the Day-Kesting process by CHEMECH Engineering Ltd., Vancouver, B.C., has indicated much higher efficiencies. This process will be described later.

ELECTROLYTIC PRODUCTION OF CHLORATE

The process of producing chlorate by electrolysis of chloride has long been established as a variation of the chlor-alkali industry. The first sodium chlorate plant in North America was in operation in 1902. The general theory involved in the production of chlorate is well known and may be summarized by the following reactions at 100% current efficiency:

$$6Cl^- = 6Cl + 6e \quad (11) ,$$

$$2H^+ = H_2 - 2e \quad (12) ,$$

$$4H_2O = 2H_2 + 4OH^- - 4e \quad (13) ,$$

$$6Cl + 3OH^- = 3HClO + 3Cl^- . \quad (14) ,$$

$$HClO + OH^- = ClO^- + H_2O \quad (15),$$

and

$$2HClO + ClO^- = ClO_3^- + 2H^+ + 2Cl^- \quad (16).$$

The first three electrolytic reactions are the same as in the chlorine-caustic production. By mixing chlorine with hydroxide in the electrolyte, the next three reactions result in the formation of chlorate. The side reactions involved are (1) the discharge of oxyanions (ClO^-, OH^-) at the anode, (2) the reduction of oxyanions (ClO^-) by nascent hydrogen at the cathode, and (3) the vaporization of hypochlorous acid and chlorine.

The formation of chlorate is favored by adding hydrochloric acid to the electrolyte, by raising the temperature, and by increasing the flow of the electrolyte. The discharge of ClO^- cannot be entirely avoided. The reduction at the cathode can be minimized by the addition of chromate which forms a protective film on the electrode surface, thereby hastening the formation of hydrogen gas. The increase of pH and temperature in the electrolyte, however, tends to release more Cl_2 and HClO. In practice, therefore, the current efficiency is generally in the range of 85-95% (8). A more detailed discussion of sodium chlorate technology is presented in a recent paper by Casson et al. (9).

ELECTROLYTIC GENERATION OF CHLORINE DIOXIDE

From the review of the present processes, the question may arise as to the possibility of generating chlorine dioxide directly by electrolysis of hydrochloric acid. Such a scheme, using sulfuric acid as the electrolyte, has been suggested by the M. W. Kellogg Company (10) as follows:

$$2Cl^- + 6H_2O = 2HClO_3 + 10H^+ + 12e \quad (17),$$

$$2H_2SO_4 = H_2S_2O_8 + 2H^+ + 2e \quad (18),$$

$$14H^{+} = 7H_2 - 14e \qquad (19),$$

$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2 \qquad (20),$$

and

$$H_2O_2 + 2HClO_3 = 2ClO_2 + O_2 + 2H_2O \qquad (21).$$

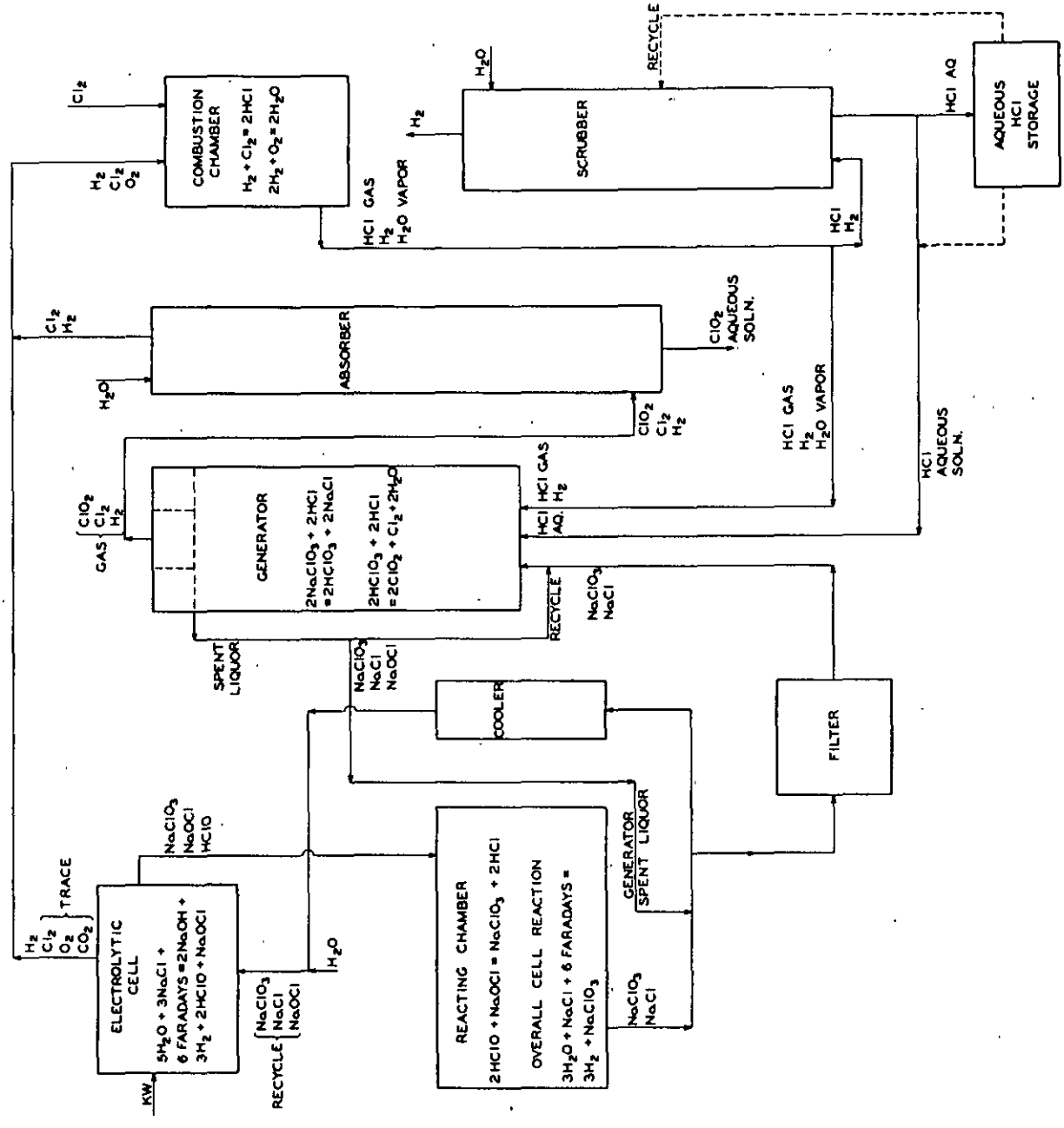
The key to this scheme is the practicability of the first anodic reaction involving the formation of hydrogen chlorate. The electrolytic production of hydrogen peroxide through persulfuric acid is a known process. The final reaction of hydrogen peroxide with hydrogen chlorate may pose additional problems. It is to be noted that this scheme requires one more faraday per mole of chlorine dioxide than the sodium chlorate method. Nevertheless, this is an interesting process as the additional ClO_2-generating equipment may be eliminated.

INTEGRATED SODIUM CHLORATE-CHLORINE DIOXIDE OPERATION

DESCRIPTION OF THE CHEMECH PROCESS

This process (11) was patented in Canada in April, 1968. It is aimed at an integrated operation for generation of chlorine dioxide from sodium chlorate electrolytically produced on site. The first CHEMECH sodium chlorate plant located at Bellingham, Washington, with a capacity of 4500 tons per year has been in satisfactory operation since its installation in 1965. The development of the chlorine dioxide-generating method on a semicommercial scale up to one ton per day was carried out at Shawinigan, Quebec, Canada, in 1967-68. The information so obtained was intended to be used for the integrated process.

The complete process uses chlorine gas as the raw chemical to produce chlorine dioxide without a liquid effluent to be disposed of. As illustrated in Fig. 1 taken from the patent, sodium chlorate is produced by electrolysis of a sodium chloride solution, the hydrogen gas evolved being partly utilized to form hydrogen chloride, and the excess hydrogen may be used as a fuel. The sodium chlorate solution is reduced by the hydrochloric acid to generate chlorine dioxide and chlorine, which are separated by preferential absorption in water. The chlorine gas so separated is recycled with its makeup for producing hydrogen chloride, which is absorbed in water and stored as an inventory. The residual solution from chlorine dioxide generation containing sodium chloride, hypochlorite, and chlorate is reused in the electrolysis, thus completing the sodium chloride cycle.


COMBUSTION CHAMBER
$H_2 + Cl_2 = 2HCl$
$2H_2 + O_2 = 2H_2O$
Cl_2
H_2 Cl_2 O_2
HCl GAS H_2 H_2O VAPOR
SCRUBBER
H_2O
H_2
RECYCLE
HCl AQ
AQUEOUS HCl STORAGE
HCl H_2
ABSORBER
Cl_2 H_2
H_2O
ClO_2 AQUEOUS SOLN.
ClO_2 Cl_2 H_2
HCl GAS H_2 H_2O VAPOR
HCl AQUEOUS SOL'N.
GENERATOR
$2NaClO_3 + 2HCl = 2HClO_3 + 2NaCl$
$2HClO_3 + 2HCl = 2ClO_2 + Cl_2 + 2H_2O$
GAS ClO_2 Cl_2 H_2
HCl HCl GAS H_2
HCl AQ.
RECYCLE
$NaClO_3$ NaCl
SPENT LIQUOR
$NaClO_3$ NaCl NaOCl
COOLER
FILTER
GENERATOR SPENT LIQUOR
REACTING CHAMBER
$2HClO + NaOCl = NaClO_3 + 2HCl$
OVERALL CELL REACTION
$3H_2O + NaCl + 6$ FARADAYS $= 3H_2 + NaClO_3$
$NaClO_3$ NaCl
$NaClO_3$ NaOCl HClO
ELECTROLYTIC CELL
$5H_2O + 3NaCl + 6$ FARADAYS $= 2NaOH + 3H_2 + 2HClO + NaOCl$
TRACE
H_2 Cl_2 O_2 CO_2
KW
RECYCLE $NaClO_3$ NaCl NaOCl
H_2O

The stoichiometric relations of the integrated process are:

$$NaCl + 3H_2O + 6 \text{ faradays} = NaClO_3 + 3H_2 \quad (22),$$

$$H_2 + Cl_2 = 2HCl \quad (23),$$

$$NaClO_3 + HCl = NaCl + HClO_3 \quad (24),$$

and

$$HClO_3 + HCl = ClO_2 + \frac{1}{2} Cl_2 + H_2O \quad (25).$$

Then the overall balance of chemicals and electricity may be represented by

$$\frac{1}{2} Cl_2 + 2H_2O + (6 \text{ faradays}) = ClO_2 + 2H_2 \quad (26).$$

As far as the electrolysis of sodium chloride is concerned, the minimum decomposition potential at concentrations prevailing in practice is taken to be 2.3 volts. At 100% current efficiency the required electricity based on Faraday's law is 696 amp.-hr./lb. $NaClO_3$. Therefore, the theoretical energy requirement is 1.6 kw.-hr. per lb. of $NaClO_3$, which is equivalent to 2.4 kw.-hr. per lb. of ClO_2 at 100% efficiency of generation.

According to the overall material balance, the requirement of chlorine is 0.526 lb. for 1 lb. of chlorine dioxide. The overall reaction (26) necessitates absorption of 4310 B.t.u. per lb. of ClO_2 at 25°C. and 1 atm. However, if the hydrogen gas is burned and condensed into water, it can supply 3650 B.t.u. The net heat required for the generation of ClO_2 is simply its heat of formation, which is 660 B.t.u./lb.

PRODUCTION OF SODIUM CHLORATE

The CHEMECH electrolytic cell is of the bipolar type, using graphite electrodes both as anode and cathode. At the Bellingham plant (12) each cell is approximately 5 ft. wide, 15 ft. long, and 6 ft. high. The graphite plates are

closely spaced in the cell, which is flooded by the electrolyte to limit the gas space and to submerge the internal electrical connections. A battery of five cells is used with one additional cell for alternation. The graphite is vacuum-impregnated with linseed oil for a longer life. Approximately 10 tons of graphite are required for one cell. The life of the electrodes is about one year.

The electrolyte is a saturated solution of sodium chloride. Calcium salts are removed in the purification process. Hydrochloric acid is added to adjust the pH of the electrolyte, and sodium dichromate for the protection of the cathode surface.

The electrolysis is carried out in the temperature range 40-45°C. and in the pH range of 6.2-6.4. While high temperatures (60-70°C.) favor the formation of chlorate, the graphite consumption becomes excessive because of the attack on the electrode by the oxyanions. The release of oxygen at the anode and the evaporation of chlorine and hypochlorous acid also increase with temperature. A high pH favors oxygen release and a low pH chlorine evolution.

The a.c. power supply is converted to d.c. by a silicon diode rectifier and is fed to the cells through aluminum bus bars. Each cell requires approximately 95 volts at the rated capacity of 8000 amp. The voltage at the electrodes is 3.5 volts and the current efficiency is 88%. The overall energy requirement is 5400-6000 kw.-hr. per ton of sodium chlorate. The net energy efficiency is, therefore, about 59-65%, which is comparable to those of chlorine-caustic production.

The rate of the overall process is controlled by the reaction of hypochlorous acid and hypochlorite ions. One or two reactors are provided to complete the reaction. The partially reacted electrolyte flows to these reactors where

the hydrogen gas is separated at the top. A large part of the exit liquor is pumped through a heat exchanger to be cooled to 30-35°C. and with the addition of NaCl is recycled to the cells. The finished liquor containing 40% $NaClO_3$ and 6.5% NaCl is filtered with a filter aid to remove the graphite particles and sent to a storage tank.

The material of construction in contact with chlorate is preferably titanium. PVC or Saran may be used in less critical areas. The explosion hazard is minimized by limiting the gas space and avoiding contamination with grease. The system is provided with automatic shutdown and alarm devices.

GENERATION OF CHLORINE DIOXIDE

The filtered liquor mixed with the hydrochloric acid from the scrubber is fed through a recirculation line to the generator (a packed column) in which the acidified liquor is brought into intimate contact with the hydrogen chloride, hydrogen, and water vapor mixture from the combustion chamber. The hot gases are compressed and pressure regulated by recirculation through a compressor, the excess being sent to the scrubber in which the hydrogen gas is separated from the hydrochloric acid. In the generator the gas stream containing chlorine dioxide and chlorine passes through an entrainment separator to the absorber where chlorine dioxide is dissolved in water with a small amount of chlorine. The exit gases containing chlorine flow to the combustion chamber to be burned with excess hydrogen from the reactor. The effluent liquor from the generator is returned to the electrolytic system through the cooler.

An example of a small-scale experiment is given in the patent as follows:

Feed	$NaClO_3$	600 g./l.
Effluent	$NaClO_3$	575 g./l.
	NaCl	110 g./l.
Temperature		50°C.
Partial pressure of Cl_2		40 mm. Hg
Chlorine consumption		0.64 lb./lb. ClO_2
Power consumption		3.85 kw.-hr./lb. ClO_2
Chlorine in ClO_2 solution		0.10 lb./lb. ClO_2

The pilot-plant operation in Shawinigan indicated that the efficiency of generation is highly dependent on the operating temperature and the chlorate/chloride ratio. It may vary from nearly zero up to 95%. The details of operation have not been disclosed.

COST OF GENERATION

For a 50-ton/day chlorine dioxide plant integrated with sodium chlorate production, CHEMECH supplied the following preliminary specifications:

1. Capital. The capital requirements including royalties are estimated to be $7.5 million for the integrated plant, of which amount $5.5 million are for 87.5 tons/day chlorate production and $2.0 million for 50 tons/day chlorine dioxide generation. Operating by 350 days, the yearly production of chlorate is 30,600 tons, and that of chlorine dioxide 17,500 tons. The efficiency of conversion is 90%. The capital costs for the CHEMECH process appear to be somewhat high, as may be seen from the following comparison:

	Capital per Daily Ton	
	CHEMECH	Others (9)
$NaClO_3$ plant	$63,000	$52,000
ClO_2 plant	$40,000	$33,000

Taking the CHEMECH figures, the depreciation at 10% a year amounts to $43 per ton of chlorine dioxide. Adding 6% interest, the total capital costs become $69 per ton.

2. Electricity. The overall energy requirement is 11,000 kw.-hr. per ton of chlorine dioxide. At a conservative estimate of 6 mils/kw.-hr., the electricity cost is $66 per ton. For favorable locations, such as Bellingham, the charge may be as low as 2.5 mils, which would reduce the energy cost to $28 per ton. A reasonable average would be 4 mils or $44 per ton.

3. Chlorine. With the recycling feature of the integrated process, the chlorine requirement is taken to be the stoichiometric ratio of 0.526:1 (Cl_2:ClO_2). At the purchase price of $60 per ton, the chlorine cost is $32 per ton of ClO_2. This cost may be reduced appreciably if the plant is integrated with chlorine-caustic production.

4. Materials. Graphite consumption is another major item. It is conservatively estimated at 26 lb. per ton of chlorine dioxide, and could be as low as 20 lb. At the former figure the graphite cost ($0.50/lb.) is $13 per ton. Other materials, such as filter aid, sodium dichromate, salt makeup, chilled water, etc., may amount to about $6 per ton.

5. Manpower. Labor, supervision, and maintenance constitute a relatively low fraction of the costs because of continuous operation and automatic control. The average man-hr. should not exceed 2, costing about $12 per ton of chlorine dioxide.

The cost outlook for an integrated process is summarized in Table III for two cases. The first is a conservative estimate for a 50-ton/day plant, and the second a more optimistic projection for a 100-ton/day plant integrated with chlorine-caustic production. A cost comparison with other commercial processes is also indicated in the table.

TABLE III

SPECIFICATIONS OF CHLORINE DIOXIDE PLANT

Capacity, tons/day	50	100
Capital, $/daily ton	150,000	120,000
Electricity		
Requirement, kw.-hr./ton	11,000	10,200
Unit cost, $/kw.-hr.	0.006	0.004
Chlorine		
Requirement, ton/ton	0.526	0.526
Unit cost, $/ton	60	45
Graphite		
Requirement, lb./ton	26	22
Unit cost, $/lb.	0.50	0.45
Manpower		
Requirement, man-hr./ton	2	1.5
Unit cost, $/man-hr.	6	7

TABLE III (Contd.)

COST OF CHLORINE PRODUCTION

Capacity, tons/day	50	100
Depreciation, excluding interest	$49	$34
Electricity	66	41
Chlorine	32	24
Graphite	13	10
Other materials	6	10
Manpower	12	11
Cost per ton	178	130
Cost per lb.	0.089	0.065
Credit		
Excess hydrogen	--	--
Hot water	--	--

COMPARISON WITH OTHER PROCESSES

	CHEMECH	Others
$NaClO_3$, tons/day	87.5	68.5 (9)
On site (incl. interest), $/ton	110-120	90-100
Purchased	--	120-140
ClO_2, tons/day	50	12 (13)
$/ton	170-180	200-280[a]

[a] Full credits for by-products.

APPLICATION TO HOLOPULPING

In the present state of development, the basic chemicals required for holopulping are chlorine dioxide (containing some chlorine), sodium hydroxide, and sodium hypochlorite. The CHEMECH process produces chlorine dioxide, hydrogen, and hydrogen chloride. If, in addition, an electrolytic chlorine-caustic plant is included in the holopulping process, the chemical requirements may be made self sufficient, with a small amount of sodium chloride and chlorine as makeup.

The combined spent liquors from the various stages of wood processing contain organic materials, chiefly modified lignin and some degraded carbohydrates, in addition to the reacted inorganic chemicals which are primarily sodium and chloride ions. By evaporation and combustion of the spent liquor, the organic materials may be converted into carbon dioxide and water vapor, and the inorganic constituents into sodium chloride and sodium carbonate (Report Five). Perhaps the simplest way of treating the solid residue after combustion is to dissolve it in water, to filter off the insolubles (such as calcium compounds and carbonaceous materials), and to convert sodium carbonate into chloride by hydrogen chloride. It is hopeful that this relatively pure sodium chloride solution may be directly recycled to the electrolytic cells.

Sodium hypochlorite can be readily prepared by absorbing chlorine in the caustic solution. The excess hydrogen over the requirement of hydrogen chloride may be used as an auxiliary fuel in the combustion of the spent liquor.

In this way nearly all the necessary chemicals would be generated from the recovered sodium chloride at the expense of electricity. The product to be disposed of would be principally carbon dioxide. There will also be a dilute

aqueous stream from pulp washing to be treated and disposed of. Such a chemical generation and recovery system and other possible alternatives are being examined in some detail, and the results of the analysis will be reported later.

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